

**Dr David's**

**Chemistry Revision Themes**

**(Homework Pages:  
Questions & Answers)**

# Theme One

## Homework: Atomic Structure.

Try answering these questions the answers are on the next page.

1. (a) Write the electronic structure of rubidium (Rb).

1s<sup>2</sup>, .....

(b) In which group of the periodic table does Rb occur?

.....

(c) When the element or its salts are heated in a bunsen flame a characteristic colour is produced. Describe this colour.

.....

(d) Natural rubidium is comprised of two main isotopes. Their masses and relative abundances are, 85 (72.2%) and 87 (27.8%). Using these figures calculate the relative atomic mass of rubidium.

.....

(e) If rubidium was subjected to analysis in the mass spectrometer,

(i) how many peaks would you expect to observe?

.....

(ii) which peak would be the base peak?

.....

(iii) write symbols for the rubidium particles reaching the detector in the mass spectrometer.

(f) would you expect the first ionisation energy of rubidium to be greater than or less than that of potassium. Explain.

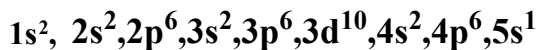
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.....

**Homework: Atomic Structure Theme.**

**Answers**

**1. (a) Write the electronic structure of rubidium (Rb).**



**(b) In which group of the periodic table does Rb occur?**

**Group 1**

**(c) When the element or its salts are heated in a bunsen flame a characteristic colour is produced. Describe this colour.**

**Red-violet**

**(d) Natural rubidium is comprised of two main isotopes. Their masses and relative abundances are, 85 (72.2%) and 87 (27.8%). Using these figures calculate the relative atomic mass of rubidium.**

**85.556**

**(e) If rubidium was subjected to analysis in the mass spectrometer,**

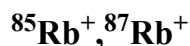
**(i) how many peaks would you expect to observe?**

**2**

**(ii) which peak would be the base peak?**

**$m/z = 85$**

**(iii) write symbols for the rubidium particles reaching the detector in the mass spectrometer.**



**(f) would you expect the first ionisation energy of rubidium to be greater than or less than that of potassium. Explain.**

**Less than. The atomic radius of Rb is larger than that of K. The outer electron of Rb is further from the nucleus. It is held less strongly and therefore easier to remove.**

# Theme Two

## Homework: Chemical Bonding & Structure.

Try answering these questions the answers are on the next page.

1. Using dot-&-cross diagrams illustrate the bonding in,

(a) magnesium oxide

(b) methane

2. Carbon dioxide has double bonds between oxygen and carbon. In each double bond, one half is a  $\pi$  bond and the other a  $\sigma$  bond. Illustrate this.

3. Why is aluminium iodide a covalent compound?

4. Illustrate the shapes of the following:

(a)  $\text{PH}_3$

(b)  $\text{SO}_4^{2-}$

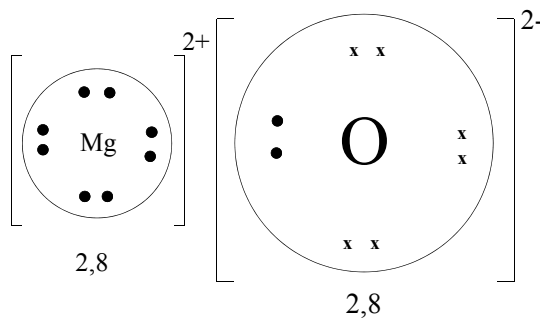
(c)  $\text{SO}_3$

## Homework: Chemical Bonding & Structure Theme.

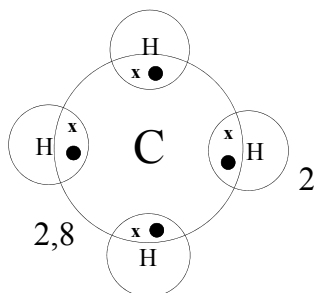
### Answers:

1. Using dot-&-cross diagrams illustrate the bonding in,

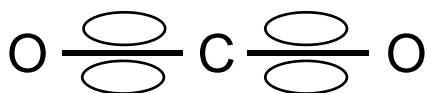
(a) magnesium oxide



(b) methane



2. Carbon dioxide has double bonds between oxygen and carbon. In each double bond, one half is a  $\pi$  bond and the other a  $\sigma$  bond. Illustrate this.

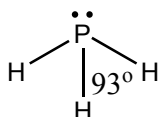


3. Why is aluminium iodide a covalent compound?

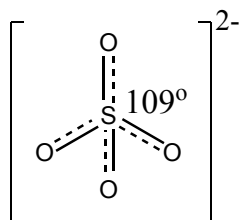
The aluminium ion is small and highly charged (+3). The iodide ion is large and negatively charged (-1); it contains a large number of electrons. The aluminium ion **polarises** the iodide ion (the iodide ion electron cloud is distorted) and electrons are shared between Al and I nuclei. The bonding is largely covalent.

4. Illustrate the shapes of the following:

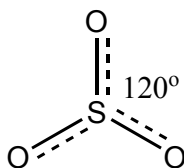
(a)  $\text{PH}_3$



(b)  $\text{SO}_4^{2-}$



(c)  $\text{SO}_3$



# Theme Three

## Homework: Formulae, Equations & Moles Theme

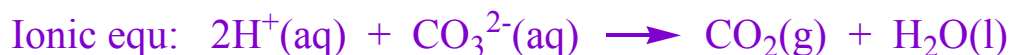
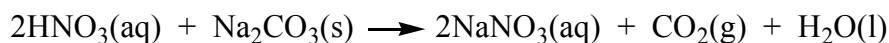
Try answering these questions the answers are on the next page.

1. Write a balanced ionic equation for the reaction between nitric acid and sodium carbonate.
2. Write the empirical, molecular and structural formulae for ethane.
3. A white crystalline solid has the % composition: C 20.00%, N 46.66%, H 6.66%. Calculate its empirical formula. Mass spectrometry gives its relative molecular mass as 60. What is its molecular and structural formulae?
4. A piece of magnesium is reacted with excess dilute sulphuric acid. The hydrogen collected occupies 50 cubic decimetres at room temperature and pressure. What is the mass of the piece of magnesium?

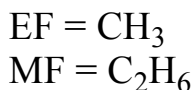
### Homework No 3: Formulae, Equations & Moles Theme

#### Answers:

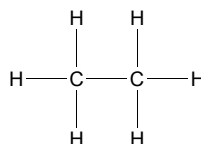
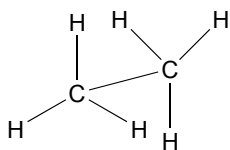
1. Write a balanced ionic equation for the reaction between nitric acid and sodium carbonate.



2. Write the empirical, molecular and structural formulae for ethane.



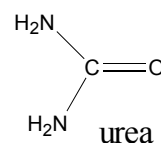
SF:



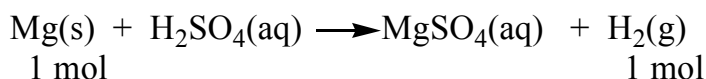
This is satisfactory although you need to be aware that the arrangement of bonds at the carbon atoms is tetrahedral (ie, 3D not planar)

3. A white crystalline solid has the % composition: C 20.00%, N 46.66%, H 6.66%. Calculate its empirical formula. Mass spectrometry gives its relative molecular mass as 60. What is its molecular and structural formulae?

C	H	N	O
20.00%	6.66%	46.66%	26.68%
20/12	6.66/1	46.66/14	26.68/16
1.67	6.66	3.33	1.67
1	4	2	1
EF = $\text{CH}_4\text{N}_2\text{O}$ = MF (based on 60!)			



4. A piece of magnesium is reacted with excess dilute sulphuric acid. The hydrogen collected occupies 50 cubic decimetres at room temperature and pressure. What is the mass of the piece of magnesium?



$$50 \text{ dm}^3 \text{ H}_2 = 50/24 \text{ mol H}_2 \text{ (2.08 mol)}$$

$$\text{mol Mg} = 2.08$$

$$\& \text{ mass Mg} = (2.08 \times 24.3) \text{ g} = 50.62 \text{ g}$$

## Theme Four

## Homework No 4: The Periodic Table Theme.

Try answering these questions the answers are on the next page.

1. (a ) Name the first four elements in each of groups 1 & 7.

- (b) Write the formula of the compound formed when the first element in group 1 reacts with the fourth element in group 7.

In a similar way, write the formula of the compound formed when the fourth element in group 1 combines with the second element in group 7.

State the type of bonding shown in these compounds.

2. The table below is an outline of the periodic table. It contains unknown elements denoted with arbitrary letters A to I (ie, not their official symbols). Identify and name these unknown elements.

																4.00 He 2																			
6.94 Li 3		9.01 Be 4														10.81 B 5		12.01 C 6		F 9		16.00 O 8		19.00 Ne 10		20.18 Na 11									
A 12		24.31 Mg 12														26.98 Al 13		28.09 Si 14		30.97 P 15		32.07 S 16		35.45 Cl 17		I 53									
39.10 K 19		40.08 Ca 20		44.96 Sc 21		47.87 Ti 22		50.94 V 23		52.00 Cr 24		54.94 Mn 25		G 26		58.93 Co 27		58.69 Ni 28		63.55 Cu 29		65.39 Zn 30		69.72 Ga 31		72.64 Ge 32		74.92 As 33		78.96 Se 34		C 36		83.80 Kr 36	
85.47 Rb 37		87.62 Sr 38		88.91 Y 39		91.22 Zr 40		92.91 Nb 41		95.94 Mo 42		98 Tc 43		101.07 Ru 44		102.91 Rh 45		106.42 Pd 46		107.87 Ag 47		112.41 Cd 48		114.82 In 49		B 51		121.76 Sb 52		127.60 Te 53		126.90 Xe 54		131.29 I 55	
132.91 Cs 55		E 56		138.91 La 57		178.49 Hf 72		180.95 Ta 73		D 74		186.21 Re 75		190.23 Os 76		192.22 Ir 77		195.08 Pt 78		H 80		200.59 Hg 80		204.38 Tl 81		207.2 Pb 82		208.98 Bi 83		209 Po 84		210 At 85		222 Rn 86	
223 Fr 87		226.03 Ra 88		227.03 Ac 89		261 Rf 104		262 Db 105		266 Sg 106		264 Bh 107		277 Hs 108		278 Mt 109		271 Ds 110		272 Rg 111															

3. As you move across period 3 from left to right the atom size decreases. Explain why this happens.

4. Explain why element C (in the table above) has a much higher melting point than krypton (they are next to one another in the table). (Mp's: C:  $-7^{\circ}\text{C}$ , Kr:  $-157^{\circ}\text{C}$ )

5. Write the electronic structure of Po.

6. How does the 1st ionisation energy of elements in a group vary as the group is descended? Explain.



## Answers:

**Group 1:** lithium, sodium, potassium, rubidium. **Group 7:** fluorine, chlorine, bromine, iodine.

In a similar way, write the formula of the compound formed when the fourth element in group 1 combines with the second element in group 7.  $\text{RbCl}$

ionic

I = argon

[illegible]

From Na to Ar there is a gradual increase in nuclear charge. From Na to Ar electrons are filling the third shell and experience similar shielding. There is a regular contraction in overall atom size, from Na to Cl, as the nuclear charge increases and the electrons are drawn in towards the nucleus.

Element C is bromine. Bromine is diatomic. A bromine molecule contains more electrons than a krypton atom and in the solid state bromine molecules experience stronger intermolecular bonding (greater van der Waals attraction) than krypton atoms. More energy is required to overcome the van der Waals attraction and separate the molecules in solid bromine than to separate the atoms in solid krypton. The melting point of bromine is, therefore, higher than that of krypton.

$$[\text{Xe}], 4f^{14}, 5d^{10}, 6s^2, 6p^4$$

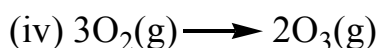
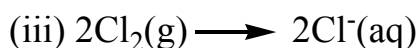
The 1st ionisation energy of elements in a group decreases as the group is descended. This is because the atoms are increasing in size (increasing atomic radius) as the shielding effect balances the increase in nuclear charge. The outer electrons are becoming further removed from the nucleus and easier to remove from the influence of the nucleus.

# Theme Five

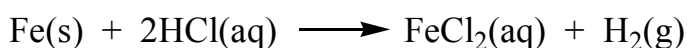
## Homework No 5: Oxidation & Reduction

Try answering these questions the answers are on the next page.

1. Which of the following involve oxidation?



2. Is the following a redox reaction? Explain.



3. Magnesium burns vigorously in air. Write a balanced equation and explain, in terms of oxidation numbers, whether it is a redox reaction.

4. Bubbling chlorine into colourless potassium bromide solution produces a dark red solution.

Write a balanced ionic equation for the reaction occurring and explain, in terms of electron transfer, why it is a redox reaction.

5. Metallic copper reacts with aqueous silver ions to give metallic silver and copper(II) ions. Using oxidation numbers, deduce the balanced ionic equation for this reaction and show that it is a redox reaction.

## Homework No 5: Oxidation & Reduction

### Answers:

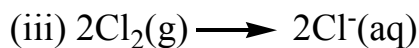
1. Which of the following involve oxidation?



oxidation of  $\text{Fe}^{2+}$

reduction of PbO

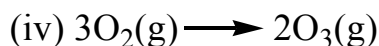
reduction of  $\text{Cl}_2$



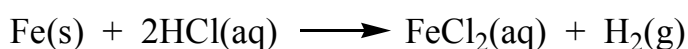
disproportionation

(in  $\text{O}_3$  can assume that the atoms have

oxidation numbers -2(one atom) & +1 (two atoms))



2. Is the following a redox reaction? Explain.



Yes.

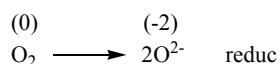
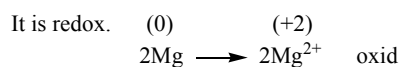
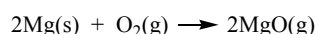
(0) (+2)

$\text{Fe} \longrightarrow \text{Fe}^{2+}$  oxid. - increase in oxid. no.

(+1) (0)

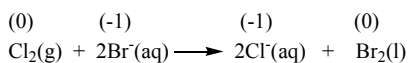
$2\text{H}^+ \rightarrow \text{H}_2$  reduc. - decrease in oxid. no.

3. Magnesium burns vigorously in air. Write a balanced equation and explain, in terms of oxidation numbers, whether it is a redox reaction.



4. Bubbling chlorine into colourless potassium bromide solution produces a dark red solution.

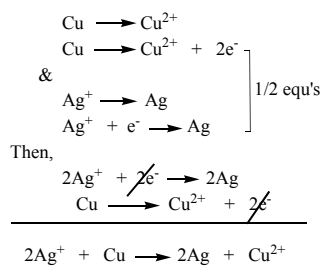
Write a balanced ionic equation for the reaction occurring and explain, in terms of electron transfer, why it is a redox reaction.



$\text{Cl}_2$  reduced because each chlorine atom gains an electron

$\text{Br}^-$  oxidised because each bromide ion loses an electron

5. Metallic copper reacts with aqueous silver ions to give metallic silver and copper(II) ions. Using oxidation numbers, deduce the balanced ionic equation for this reaction and show that it is a redox reaction.



# Theme Six

## Homework No 6: Inorganic Chemistry.

Try answering these questions the answers are on the next page.

1. 2 litres of chlorine gas, measured at room temperature and pressure, is bubbled into an aqueous solution of excess KI.

Describe what would be observed:

A 100 cm<sup>3</sup> of tetrachloromethane is added to the above mixture. After shaking and allowing to settle, two liquid layers form. Describe and explain the result.

Calculate the amount (moles) of iodine displaced in the above reaction.

How may solid iodine be isolated from the above mixture?

2. An s-block element was reacted with chlorine and the white crystalline solid dissolved in water. A platinum wire was dipped into the solution and held in a hot bunsen flame. A pale green colour was observed.

The above aqueous solution was tested with, (i) dilute sodium hydroxide solution and (ii) dilute sulphuric acid.

(a). Identify the s-block element.

(b). Describe and explain what happens when the dilute sodium hydroxide solution is added.

(c). Describe and explain what happens when the dilute sulphuric acid acid is added.

3. Write the formulae of the chlorides of the elements in period 3.

Explain how they behave when added to water.

4. Write the electronic structure of the copper(II) ion.

Draw a structural formula for the hydrated copper(II) ion.

Write equations for two reactions which may be used to test for the copper(II) ion.

## Homework No 6: Inorganic Chemistry

### Answers:

1. 2 litres of chlorine gas, measured at room temperature and pressure, is bubbled into an aqueous solution of excess KI.

Describe what would be observed: *The colourless KI solution would immediately start turning brown due to the formation of iodine.*

A 100 cm<sup>3</sup> of tetrachloromethane is added to the above mixture. After shaking and allowing to settle, two liquid layers form. Describe and explain the result. *Tetrachloromethane is immiscible with water and forms a bottom layer since it is denser than water. It also preferentially dissolves the iodine to give a purple coloured solution containing iodine mols.*

Calculate the amount (moles) of iodine displaced in the above reaction.

$$2/24 \text{ mol } (0.083 \text{ ' mol})$$

How may solid iodine be isolated from the above mixture?

*Allow the solvent (tetrachloromethane) to evaporate in a fume cupboard. (or distil off under reduced pressure in a rotary evaporator.)*

*NB: In practice you would be unlikely to use tetrachloromethane since there is some evidence that the substance is carcinogenic. A safer solvent to use in the lab is dichloromethane. This too is immiscible with water and heavier than water and readily dissolves iodine giving a purple solution*

2. An s-block element was reacted with chlorine and the white crystalline solid dissolved in water. A platinum wire was dipped into the solution and held in a hot bunsen flame. A pale green colour was observed.

The above aqueous solution was tested with, (i) dilute sodium hydroxide solution and (ii) dilute sulphuric acid.

(a). Identify the s-block element. *Barium*

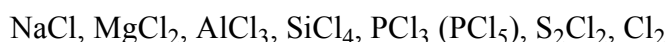
(b). Describe and explain what happens when the dilute sodium hydroxide solution is added.

*No change. Barium hydroxide is soluble in water.*

(c). Describe and explain what happens when the dilute sulphuric acid is added.

*A white precipitate of barium sulphate is formed. Barium sulphate is sparingly soluble in water.*

3. Write the formulae of the chlorides of the elements in period 3.



Explain how they behave when added to water.

*Sodium chloride dissolves to give a colourless solution. Similarly with magnesium chloride.*

*Aluminium chloride also dissolves but is then hydrolysed to give a cloudy, white, solution.*

*The cloudyness is due to insoluble aluminium hydroxide.*

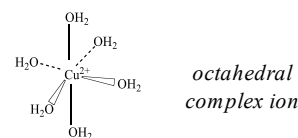
*Silicon, phosphorus and sulphur chlorides are highly reactive towards water. Silicon chloride is hydrolysed to the hydrated oxide. Phosphorus chlorides are hydrolysed to a mixture of oxychloride and phosphoric acid.*

*Sulphur chlorides are hydrolysed to a mixture of sulphur dioxide, hydrochloric acid and sulphur.*

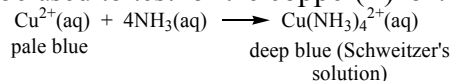
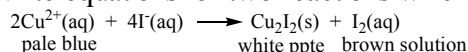
*Chlorine reacts forming chlorine water which contains dissolved chlorine, HOCl(aq) & HCl(aq)*

4. Write the electronic structure of the copper(II) ion.  $[\text{Ar}], 3d^9$

Draw a structural formula for the hydrated copper(II) ion.



Write equations for two reactions which may be used to test for the copper(II) ion.



# Theme Seven

## Homework No 7: Chemical Equilibria.

Try answering these questions the answers are on the next page.

1. If you were explaining *dynamic equilibrium* to a colleague, what would you wish to emphasise to ensure that he/she understands the concept?
2. Sketch a graph showing how the concentrations of reactants and products, in a reversible reaction, may vary from the time of mixing the reactants to the time of dynamic equilibrium.
3. Write a chemical equation to represent the Haber process.

State and explain optimum conditions for a product yield in excess of 90%.

4. In a closed, glass, container, at room temperature and pressure, *chlorine water* is a system in dynamic equilibrium. Write a chemical equation to represent this system.

State how the position of equilibrium could be changed without opening the container.

5. A solution of potassium dichromate provides an equilibrium mixture.

State and explain what would be observed if, (i) dilute sodium hydroxide was added slowly to excess, (ii) dilute hydrochloric acid was added slowly to excess.

Potassium dichromate is a powerful oxidising agent. Provide an example of this property by writing a suitable chemical equation and stating what is being oxidised and what is being reduced.

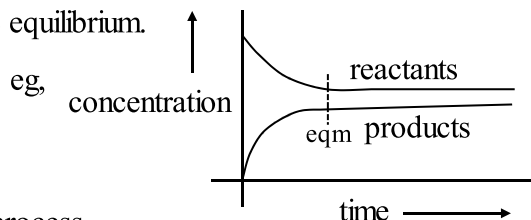
6. How is sulphur trioxide made commercially? Write a chemical equation and state the conditions used.

## Homework No 7: Chemical Equilibria. Answers:

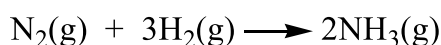
1. If you were explaining *dynamic equilibrium* to a colleague, what would you wish to emphasise to ensure that he/she understands the concept?

*In a reaction mixture, at equilibrium, the molecules of reactants and products are rushing about in a random fashion. As they collide, reaction sometimes occurs. However, the forward and backward reactions occur at the same rate and the amounts of reactants and products remain constant.*

2. Sketch a graph showing how the concentrations of reactants and products, in a reversible reaction, may vary from the time of mixing the reactants to the time of dynamic equilibrium.



3. Write a chemical equation to represent the Haber process.



State and explain the optimum conditions for a product yield in excess of 90%.

*High pressure (600 atm), low temperature 200°C.*

*The left to right reaction is exothermic therefore, in order to produce ammonia, the temperature should be at a minimum. The left to right reaction involves a reduction in volume (fewer mols) and therefore a high pressure would favour this change (Le Chatelier's principle).*

4. In a closed, glass, container, at room temperature and pressure, *chlorine water* is a system in dynamic equilibrium. Write a chemical equation to represent this system.



State how the position of equilibrium could be changed without opening the container.

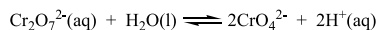
*Heating up or cooling down the mixture would shift the equilibrium, altering the amounts of reactants and products.*

*(Exposing to UV light would introduce oxygen resulting from the decomposition of HOCl(aq). You would no longer have the original chlorine water system!)*

5. A solution of potassium dichromate provides an equilibrium mixture.

State and explain what would be observed if, (i) dilute sodium hydroxide was added slowly to excess, (ii) dilute hydrochloric acid was added slowly to excess.

*(i) The orange colour would gradually disappear. Hydroxide ion removes hydrogen ion and the equilibrium adjusts with a shift from left to right. In so doing the dichromate ion concentration is reduced and hydrogen ion re-introduced.*



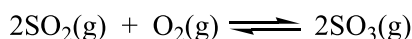
*(ii) The orange colour would be restored. Introduction of hydrogen ion results in the equilibrium shifting to the left since, in so doing, excess hydrogen ion is combined with chromate ion to give dichromate ion and water.*

Potassium dichromate is a powerful oxidising agent. Provide an example of this property by writing a suitable chemical equation and stating what is being oxidised and what is being reduced.

*Dichromate ion in dilute sulphuric acid is a popular oxidising agent in organic chemistry. It oxidises primary alcohols to aldehydes and thence to carboxylic acids. eg,  $\text{CH}_3\text{CH}_2\text{OH} + (\text{O}) \longrightarrow \text{CH}_3\text{CHO} + (\text{O}) \longrightarrow \text{CH}_3\text{COOH}$  Dichromate ion is reduced to chromium(III) ion & water. ethanol from oxidising agent ethanal ethanoic acid*

6. How is sulphur trioxide made commercially? Write a chemical equation and state the conditions used.

Sulphur trioxide is manufactured by reacting sulphur dioxide with oxygen. The pressure used is just in excess of 1 atm and the temperature, 450°C. Vanadium(V) oxide is the catalyst.



# Theme Eight

## Homework No 8: Chemical Energetics

Try answering these questions, the answers are on the following pages.

1. Define, enthalpy of neutralisation.

50 cm<sup>3</sup> of 4M sodium hydroxide solution were introduced into a plastic cup.

The temperature of the solution was measured. 50 cm<sup>3</sup> of 4M hydrochloric acid (at the same initial temperature as the alkali) was added to the plastic cup, the mixture was stirred and the highest temperature recorded.

Initial temperature of the alkali (and the acid) = 20.0°C

Final temperature of the mixture = 47.0°C

(i) What was the temperature rise? (ii) Is the reaction exothermic or endothermic?

(iii) Calculate the enthalpy change?

(iv) How many moles of alkali (and acid) were neutralised?

(v) Calculate the enthalpy change per mole.

Write a balanced equation for the reaction which is responsible for the enthalpy change.

If the acid is replaced by ethanoic acid (same concentration) the enthalpy change is different. Explain.

2. A small crucible was charged with 0.5g of propan-1-ol. The crucible was placed under a copper beaker (mass = 100g) containing 100 cm<sup>3</sup> of water at 19.0°C. The alcohol was lit and allowed to burn immediately below the beaker. The alcohol was allowed to burn away completely and the final temperature of the water was 55°C.

Specific heat capacity of water = 4.2 Jg<sup>-1</sup>K<sup>-1</sup>. Specific heat capacity of copper = 0.42 Jg<sup>-1</sup>K<sup>-1</sup>

(i) State the temperature rise. (ii) Calculate the enthalpy change of the copper beaker.

(iii) Calculate the enthalpy change of the water in the beaker.

(iv) Calculate the **total** enthalpy change.

(v) Calculate the standard enthalpy of combustion of propan-1-ol assuming measurements were made at 1 atm.

Formula of propan-1-ol = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH

(vi) Write a balanced chemical equation for the complete combustion of 1 mole of propan-1-ol.

(vii) Suggest ways of improving this experiment to make the results more consistent and to provide a more accurate result.



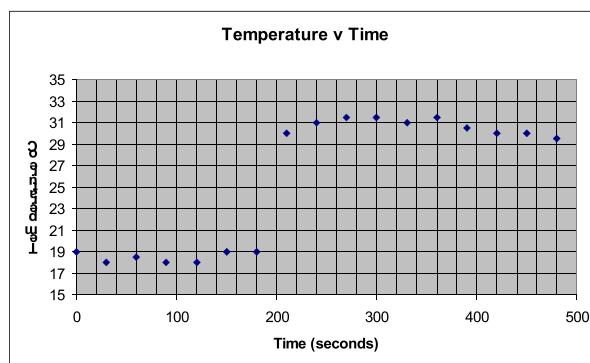
3. Copper(II) sulphate solution (50 cm<sup>3</sup>, 0.25M) was poured into a polystyrene cup supported in a beaker. A thermometer was placed in the solution and the temperature measured & recorded every 30 seconds. When the temperature attained a steady value 1g of powdered zinc was added and the mixture stirred continuously for the next five minutes. The temperature was recorded every 30 seconds. The results were plotted as shown below.

Write an ionic equation for the reaction occurring between zinc atoms and hydrated copper(II) ions.

From the graph find the *corrected* temperature rise.

Assume a value of 4.2 joules per degree per cm<sup>3</sup> for the heat capacity of the reaction mixture.

Calculate the heat evolved.



Calculate the enthalpy change per mole of copper displaced from solution.

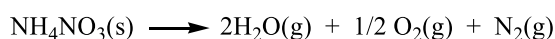
4. Given the following thermochemical data construct a reaction cycle and calculate the enthalpy of formation of ethanol.

$$\Delta H_f^\ominus \text{ carbon dioxide} = -393 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus \text{ water} = -286 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\ominus \text{ ethanol} = -1368 \text{ kJ mol}^{-1}$$

5. Ammonium nitrate is important as a fertilizer and as an ingredient of explosives. It can decompose according to the following equation.



Given the following enthalpies of formation calculate the enthalpy change for this decomposition.

$$\Delta H_f^\ominus \text{ ammonium nitrate} = -367 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus \text{ water as steam} = -242 \text{ kJ mol}^{-1}$$

Given the following entropies calculate the free energy change for the decomposition and comment on the reaction feasibility. (assume 298K)

$$S^\ominus \text{ solid ammonium nitrate} = 151 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S^\ominus \text{ water as steam} = 189 \text{ JK}^{-1}\text{mol}^{-1}$$

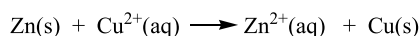
$$S^\ominus \text{ oxygen} = 205 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S^\ominus \text{ nitrogen} = 191 \text{ JK}^{-1}\text{mol}^{-1}$$

*The big problem is loss of heat directly to the surroundings. The flame and calorimeter must be protected from drafts. A lid on the calorimeter would also reduce heat loss. More sophisticated apparatus is available commercially (look in science equipment catalogues.)*

3. Copper(II) sulphate solution (50 cm<sup>3</sup>, 0.25M) was poured into a polystyrene cup supported in a beaker. A thermometer was placed in the solution and the temperature measured & recorded every 30 seconds. When the temperature attained a steady value 1g of powdered zinc was added and the mixture stirred continuously for the next five minutes. The temperature was recorded every 30 seconds. The results were plotted as shown below.

Write an ionic equation for the reaction occurring between zinc atoms and hydrated copper(II) ions.

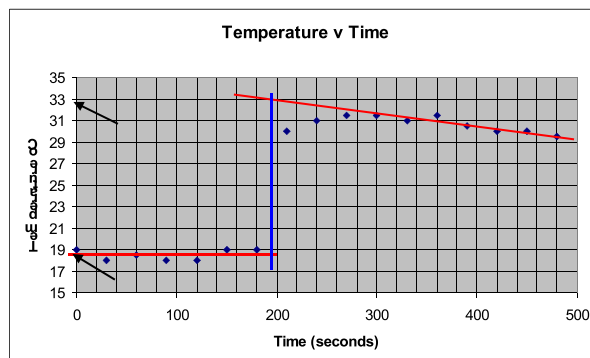


From the graph find the *corrected* temperature rise.

$$32.9 - 18.6 = 14.3\text{ }^{\circ}\text{C}$$

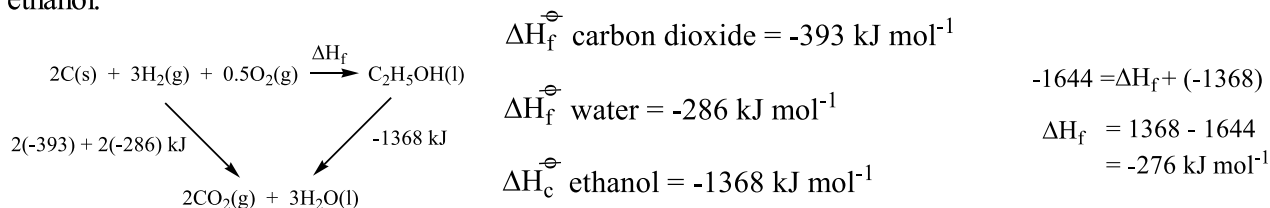
Assume a value of 4.2 joules per degree per cm<sup>3</sup> for the heat capacity of the reaction mixture.

Calculate the heat evolved.  $50 \times 4.2 \times 14.3 = 3003\text{ J}$

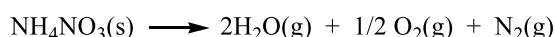


Calculate the enthalpy change per mole of copper displaced from solution.  $3003 \times 1/0.025 = 240.2\text{ kJ mol}^{-1}$

4. Given the following thermochemical data construct a reaction cycle and calculate the enthalpy of formation of ethanol.



5. Ammonium nitrate is important as a fertilizer and as an ingredient of explosives. It can decompose according to the following equation.



Given the following enthalpies of formation calculate the enthalpy change for this decomposition.

$\Delta H_f^{\ominus} \text{ ammonium nitrate} = -367\text{ kJ mol}^{-1}$ $\Delta H_f^{\ominus} \text{ water as steam} = -242\text{ kJ mol}^{-1}$	$\Delta H = 2(-242) - (-367)$ $= -484 + 367 = -117\text{ kJ mol}^{-1}$
---	--

Given the following entropies calculate the free energy change for the decomposition and comment on the reaction feasibility. (assume 298K)

$S^{\ominus} \text{ solid ammonium nitrate} = 151\text{ JK}^{-1}\text{mol}^{-1}$ $S^{\ominus} \text{ water as steam} = 189\text{ JK}^{-1}\text{mol}^{-1}$ $S^{\ominus} \text{ oxygen} = 205\text{ JK}^{-1}\text{mol}^{-1}$ $S^{\ominus} \text{ nitrogen} = 191\text{ JK}^{-1}\text{mol}^{-1}$	$\Delta S_{\text{reaction}} = 671.5 - 151 = +520.5\text{ J}$ $\Delta G = -117000 - (298 \times 520.5)$ $= -117000\text{ J} - 155109\text{ J}$ $= -272\text{ kJ mol}^{-1}$
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*This negative value indicates that the reaction is feasible (very much so!).*

# Theme Nine

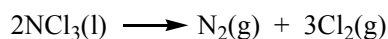
## Homework No 9: Chemical Kinetics.

Try answering these questions, the answers are on the pages which follow.

1. State four factors which control rate of reaction.

A reaction mixture comprising gaseous reactants and products is contained in a cylinder fitted with a movable piston. Pressure is applied to the piston and the reaction mixture compressed into a smaller volume. Assuming the temperature remains constant, what effect will this have on the rate of reaction?

2. Consider the following reaction,

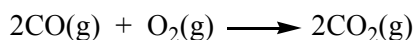


Is it possible to write the general form of the rate equation for this reaction given the balanced chemical equation? Explain.

A trace of hexane increases the rate of this reaction dramatically. What term can be applied to the hexane which describes its action on this reaction?

Draw a Maxwell-Boltzmann distribution curve and use it to help explain the action of the hexane on the rate of this reaction.

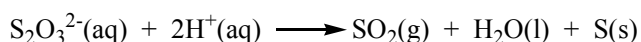
3. The oxidation of carbon monoxide, at a fixed temperature, was studied in the laboratory with the following results.



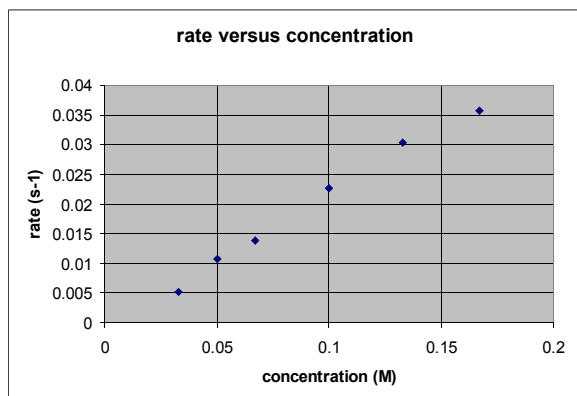
Concentration of carbon monoxide (mol dm <sup>-3</sup> )	Concentration of oxygen (mol dm <sup>-3</sup> )	Rate of formation of carbon dioxide (mol dm <sup>-3</sup> s <sup>-1</sup> )
0.002	0.001	0.0002
0.004	0.001	0.0004
0.002	0.002	0.0004

Write the general form of the rate equation for this reaction.

4. Experiments were performed to investigate the rate and order of the following reaction:



(a) The concentration of the thiosulphate solution was varied and the time taken for a given amount of sulphur to be deposited was recorded. The temperature and the concentration of hydrogen ion were kept constant. A graph was plotted of rate (reciprocal of time) against concentration.



Draw the best straight line through the points.

If you agree that the results show a straight line relationship state the order with respect to thiosulphate. Calculate the slope.

Choose a pair of rate/concentration values (from the graph) and substitute these into a general form of the rate equation, along with the rate constant, and calculate a value for the order. Does this confirm your previous statement of the order?

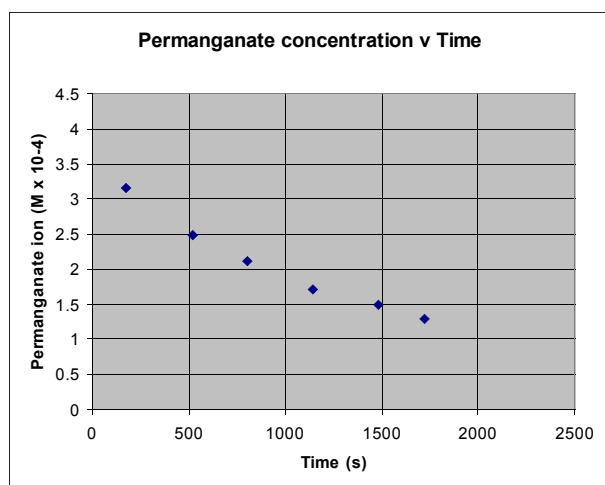
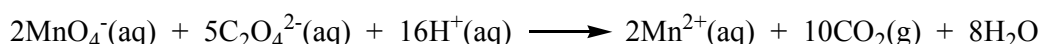
(b) In a second experiment the concentration of thiosulphate was kept constant and the hydrogen ion concentration varied. Temperature was again held constant.

Concentration of hydrogen ion (M)	Time to precipitate a fixed amount of sulphur (s)
0.167	28
0.15	24
0.13	26
0.12	26
0.10	28
0.083	31

From these results state the order with respect to hydrogen ion concentration.

Write the overall rate equation.

5. An experiment was performed to study the rate of reaction between permanganate ion and oxalate ion.



As this reaction proceeds the colour of the permanganate becomes less intense. With dilute solutions and a slight excess of oxalate the colour changes from pale purple to colourless. The concentration of permanganate at various times during the reaction can be established colorimetrically or titrimetrically (eg. adding aliquots of the reaction mixture to 5% KI solution and titrating the liberated iodine against standard thiosulphate solution).

A graph was plotted of permanganate ion concentration at various times during the course of the reaction (see adjacent). From this deduce the overall order of the reaction. Explain.

## Homework No 9: Chemical Kinetics. Answers:

1. State four factors which control rate of reaction.

*Temperature, concentration, physical state, catalyst*

A reaction mixture comprising gaseous reactants and products is contained in a cylinder fitted with a movable piston. Pressure is applied to the piston and the reaction mixture compressed into a smaller volume. Assuming the temperature remains constant, what effect will this have on the rate of reaction?

*The rate will increase because, effectively, the concentration has increased*

2. Consider the following reaction,

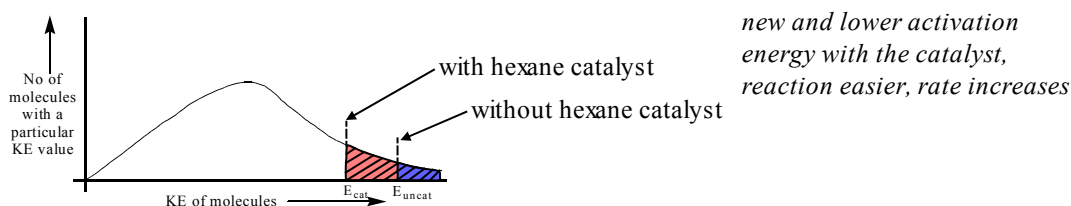


Is it possible to write the general form of the rate equation for this reaction given the balanced chemical equation?

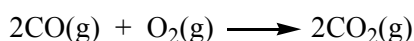
**Explain.** *No. Rate equations cannot be written by inspecting the stoichiometric equation. A reaction must be studied experimentally, in the laboratory, to provide the required data in order to establish the rate equation.*

A trace of hexane increases the rate of this reaction dramatically. What term can be applied to the hexane which describes its action on this reaction? *The hexane is acting as a catalyst.*

Draw a Maxwell-Boltzmann distribution curve and use it to help explain the action of the hexane on the rate of this reaction.



3. The oxidation of carbon monoxide, at a fixed temperature, was studied in the laboratory with the following results.

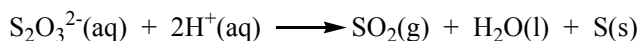


Concentration of carbon monoxide (mol dm <sup>-3</sup> )	Concentration of oxygen (mol dm <sup>-3</sup> )	Rate of formation of carbon dioxide (mol dm <sup>-3</sup> s <sup>-1</sup> )
0.002	0.001	0.0002
0.004	0.001	0.0004
0.002	0.002	0.0004

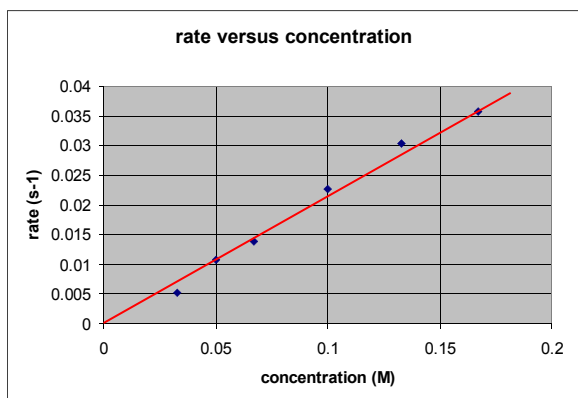
Write the general form of the rate equation for this reaction.

*double carbon monoxide concentration, rate doubles  
double oxygen concentration, rate doubles  
It follows, rate = k [CO]. [O<sub>2</sub>] ie, overall 2nd order*

4. Experiments were performed to investigate the rate and order of the following reaction:



(a) The concentration of the thiosulphate solution was varied and the time taken for a given amount of sulphur to be deposited was recorded. The temperature and the concentration of hydrogen ion were kept constant. A graph was plotted of rate (reciprocal of time) against concentration.



Draw the best straight line through the points.

If you agree that the results show a straight line relationship state the order with respect to thiosulphate. Calculate the slope.

Choose a pair of rate/concentration values (from the graph) and substitute these into a general form of the rate equation, along with the rate constant, and calculate a value for the order. Does this confirm your previous statement of the order?

*Rate proportional to thiosulphate concentration ..... 1st order*

*$k = \text{slope} = 0.213 \text{ mol dm}^3 \text{ s}^{-1}$*

*$\text{rate} = 0.213 \times [\text{thio}]^1$  .....should find agreement*

(b) In a second experiment the concentration of thiosulphate was kept constant and the hydrogen ion concentration varied. Temperature was again held constant.

Concentration of hydrogen ion (M)	Time to precipitate a fixed amount of sulphur (s)
0.167	28
0.15	24
0.13	26
0.12	26
0.10	28
0.083	31

From these results state the order with respect to hydrogen ion concentration.

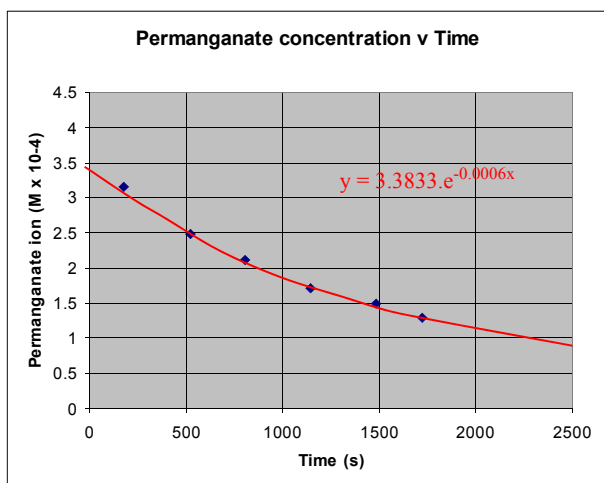
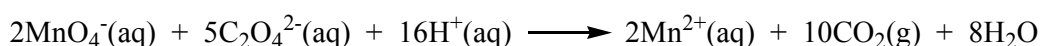
Write the overall rate equation.

*No change in rate with change in hydrogen ion concentration ..*

*..... zero order wrt hydrogen ion*

*$\text{rate} = k [\text{S}_2\text{O}_3^{2-}]^1 [\text{H}^+]^0$*

5. An experiment was performed to study the rate of reaction between permanganate ion and oxalate ion.



As this reaction proceeds the colour of the permanganate becomes less intense. With dilute solutions and a slight excess of oxalate the colour changes from pale purple to colourless. The concentration of permanganate at various times during the reaction can be established colorimetrically or titrimetrically (eg, adding aliquots of the reaction mixture to 5% KI solution and titrating the liberated iodine against standard thiosulphate solution).

A graph was plotted of permanganate ion concentration at various times during the course of the reaction (see adjacent). From this deduce the overall order of the reaction. Explain.

*Smooth exponential decay of permanganate concentration .....*

*.... overall 1st order*

*(constant half-life.... can be confirmed using equation for the line)*

# Theme Ten

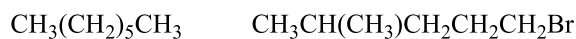
## Homework No 10: Organic Chemistry

Try answering these questions the answers are on the pages which follow.

1. The alkane, ethane, has the molecular formula,  $C_2H_6$

Draw its structural formula so as to illustrate its 3-dimensional nature and the arrangement of bonds about the carbon atoms.

2. Give systematic names for the following molecules:



3. Draw all structural formulae of alkanes having the molecular formula,  $C_6H_{14}$

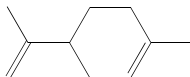
Name each one and state the type of structural isomerism they exhibit. Identify all the *secondary* carbon atoms, in the structures, with an asterisk.

4. Define the term *electrophile* and give an example of a reaction in which a named electrophile is involved.



5. Which is the most polar bond in the following structure,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ . Name this compound. Is it likely to be as chemically reactive as,  $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$ ? Explain.

6. What is the common name of this hydrocarbon?



Where is it found in nature?

How would you expect it to react with excess bromine? State the type of reaction and write the formula of the expected product.

7.  $20\text{ cm}^3$  of a gaseous hydrocarbon were exploded with  $100\text{ cm}^3$  of oxygen (this being in excess). The volume became  $80\text{ cm}^3$ . This was further reduced to  $40\text{ cm}^3$  by shaking with potassium hydroxide solution. All measurements at room temperature and pressure. Deduce the molecular formula of the hydrocarbon.

8. A quantity (1.80g) of a hydrocarbon, **A**, produces 6.16g of carbon dioxide and 1.08g of water on complete combustion. Calculate the empirical formula of **A**. Suggest, with a reason, whether you think the hydrocarbon is aliphatic or aromatic.

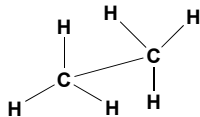
9. Draw the cis and trans forms of but-2-ene.

Write an equation for the reaction of but-2-ene with hydrogen bromide. Name the product.

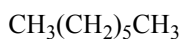
## Homework No 10: Organic Chemistry I (answers)

1. The alkane, ethane, has the molecular formula,  $C_2H_6$

Draw its structural formula so as to illustrate its 3-dimensional nature and the arrangement of bonds about the carbon atoms.



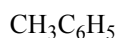
2. Give systematic names for the following molecules:



*heptane*



*1-bromo-4-methylpentane*



*methylbenzene*



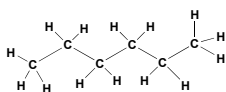
*1,2,3-trichloropropane*



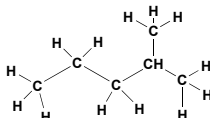
*2-bromopropan-1-ol*

3. Draw all structural formulae of alkanes having the molecular formula,  $C_6H_{14}$

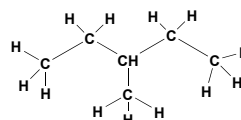
Name each one and state the type of structural isomerism they exhibit. Identify all the *secondary* carbon atoms, in the structures, with an asterisk.



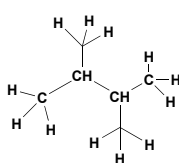
*hexane*



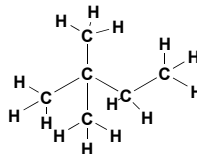
*2-methylpentane*



*3-methylpentane*



*2,3-dimethylbutane*



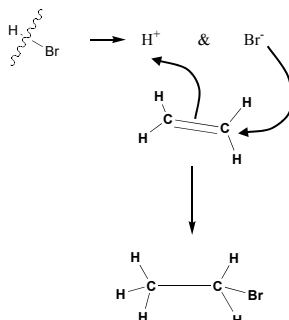
*2,2-dimethylbutane*

4. Define the term *electrophile* and give an example of a reaction in which a named electrophile is involved.

*An atom or group which can form a covalent bond by accepting an electron pair.*

*eg,*

*Addition of HBr to ethene in which hydrogen ion acts as the electrophile, accepting a pair of pi bond electrons.*

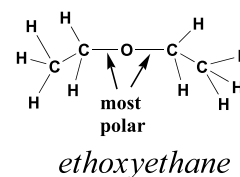


5. Which is the most polar bond in the following structure,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ . Name this compound.

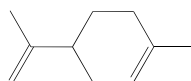
Is it likely to be as chemically reactive as,  $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$ ? Explain.

*No. Butan-2-ol contains a reactive, polar, secondary alcohol group.*

*The ether, ethoxyethane, has relatively strong, weakly polar, bonds & is less reactive than the alcohol.*



6. What is the common name of this hydrocarbon?



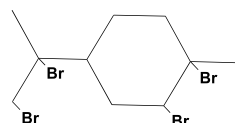
*limonene*

Where is it found in nature?

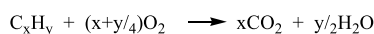
*In essential oils. It is present in the oil from orange peel.*

How would you expect it to react with excess bromine? State the type of reaction and write the formula of the expected product.

*Undergoes an addition reaction.*



7.  $20 \text{ cm}^3$  of a gaseous hydrocarbon were exploded with  $100 \text{ cm}^3$  of oxygen (this being in excess). The volume became  $80 \text{ cm}^3$ . This was further reduced to  $40 \text{ cm}^3$  by shaking with potassium hydroxide solution. All measurements at room temperature and pressure. Deduce the molecular formula of the hydrocarbon.



$$20 \text{ vol} \quad 20(x+y/4) \text{ vol} \quad 20x \text{ vol}$$

$$\begin{aligned} \text{volume of CO}_2 &= 40 \text{ cm}^3 \\ &= 20x \text{ cm}^3 \end{aligned}$$

$$\text{then, } x = 2$$

$$\text{volume of O}_2 \text{ used} = 100 - 40 = 60 \text{ cm}^3$$

$$60 = 20(x + y/4) = 20(2 + y/4)$$

$$\text{from which, } y = 4$$

$$\text{ie, } \text{C}_2\text{H}_4$$

8. A quantity (1.80g) of a hydrocarbon, **A**, produces 6.16g of carbon dioxide and 1.08g of water on complete combustion. Calculate the empirical formula of **A**. Suggest, with a reason, whether you think the hydrocarbon is aliphatic or aromatic.

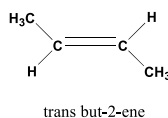
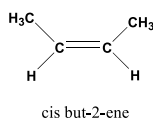
$$\text{mass of carbon in the hydrocarbon} = 12/44 \times 6.16 = 1.68\text{g}$$

$$\text{mass of hydrogen in the hydrocarbon} = 2/18 \times 1.08 = 0.12\text{g}$$

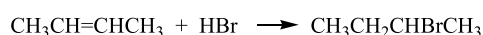
C	:	H
1.68		0.12
1.68/12		0.12/1
0.14		0.12
1.167		1
7		6
EF = $\text{C}_7\text{H}_6$		

High carbon to hydrogen ration, therefore highly unsaturated, probably aromatic eg,  $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$

9. Draw the cis and trans forms of but-2-ene.



Write an equation for the reaction of but-2-ene with hydrogen bromide. Name the product.



2-bromobutane

# Theme Eleven

## Homework No 11: Organic Chemistry

Try answering these questions the answers are on the pages which follow.

1. How could you show that 1-bromobutane undergoes hydrolysis more readily than 1-chlorobutane?

Why is it more difficult to hydrolyse 1-chlorobutane than to hydrolyse 1-bromobutane?

2. Write equations to show how bromomethane could be converted to ethanoic acid.

3. Write equations to show how 1-iodopropane can be converted to butan-1-amine

4. It is suspected that a colourless organic liquid is ethanol. Describe some tests that could be applied to the liquid to confirm that it is ethanol.

5. How could 1-bromopropane be converted to 2-bromopropane?

6. The % composition of a halogenohydrocarbon of relative molecular mass 64.5 is:

C = 37.2%, H = 7.8%, Cl = 55.0%

Determine the empirical and molecular formulae of the compound.

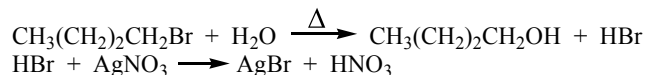
7. By applying suitable measurements and tests explain how you would distinguish butan-1-ol from butan-2-ol.

8. An unsaturated alcohol containing carbon, hydrogen and oxygen only, reacts with bromine ( $\text{Br}_2$ ) in a 1:1 molar ratio. With acidified potassium dichromate it forms an unsaturated methyl ketone. It has five carbon atoms and does not exhibit geometrical isomerism. Draw a structure for the unsaturated alcohol. Provide some reasoning.

## Homework No 11: Organic Chemistry II (answers)

1. How could you show that 1-bromobutane undergoes hydrolysis more readily than 1-chlorobutane?

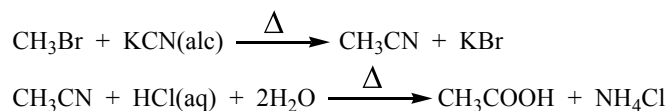
Add 2 ml of aq-alc silver nitrate solution to a test tube. Add 3 drops of haloalkane and stir. Place the tube in a beaker of hot water and monitor the appearance of the solution with time. A precipitate of silver halide forms more quickly in the case of 1-bromobutane indicating more rapid hydrolysis.



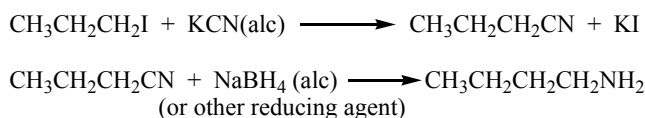
Why is it more difficult to hydrolyse 1-chlorobutane than to hydrolyse 1-bromobutane?

The C-Cl bond energy is greater than the C-Br bond energy therefore hydrolysis of  $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Cl}$  occurs more slowly.

2. Write equations to show how bromomethane could be converted to ethanoic acid.

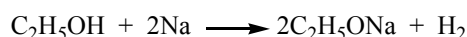


3. Write equations to show how 1-iodopropane can be converted to butan-1-amine



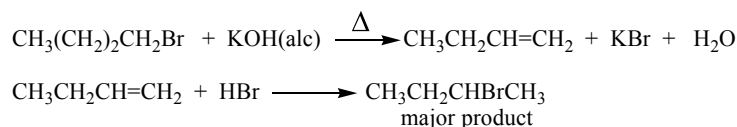
4. It is suspected that a colourless organic liquid is ethanol. Describe some tests that could be applied to the liquid to confirm that it is ethanol.

(i) Add a small piece of sodium metal. Observe the evolution of hydrogen.



(ii) Warm the liquid with potassium dichromate solution acidified with dil. sulphuric acid. The solution changes colour, orange to green as the alcohol is oxidised. (iii) Collect some of the vapour from (ii) and test with Tollens reagent. A silver mirror is produced confirming ethanal and hence the original ethanol.

5. How could 1-bromopropane be converted to 2-bromopropane?



6. The % composition of a halogenohydrocarbon of relative molecular mass 64.5 is:

C = 37.2%, H = 7.8%, Cl = 55.0%

Determine the empirical and molecular formulae of the compound.

C	:	H	:	Cl
37.2		7.8		55.0
37.2/12		7.8/1		55.0/35.5
3.1		7.8		1.549
2.0		5.0		1

ie, EF = C<sub>2</sub>H<sub>5</sub>Cl  
formula mass = 64.5  
therefore, EF = MF

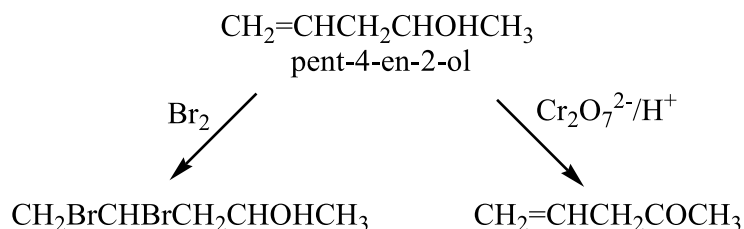
7. By applying suitable measurements and tests explain how you would distinguish butan-1-ol from butan-2-ol.

Measure bp's and compare with literature values (butan-1-ol = 118°C,  
butan-2-ol = 100°C).

Oxidation of butan-1-ol with dichromate & sulphuric acid gives butanal and  
then butanoic acid. Test the aldehyde with 2,4-DNP & Tollen's & Fehling's reagents.  
Test for acid with litmus & esterification.

Butan-2-ol gives the ketone, butanone (negative result with Tollen's & Fehling's).

8. An unsaturated alcohol containing carbon, hydrogen and oxygen only, reacts with bromine (Br<sub>2</sub>) in a 1:1 molar ratio. With acidified potassium dichromate it forms an unsaturated methyl ketone. It has five carbon atoms and does not exhibit geometrical isomerism. Draw a structure for the unsaturated alcohol. Provide some reasoning.



If the double bond is terminal there are no geometrical isomers. The secondary alcohol group is oxidised to a ketone.

# Theme Twelve

## Homework No 12: Organic Chemistry III

Try answering these questions the answers are on the pages which follow.

1. Write a structural formula for, E-1-bromo-2-chloropropene.
2. Draw structural formulae for the enantiomers of butan-2-ol. Indicate on your formulae which is the S-form and which the R-form.
3. Draw a structural formula for carvone. Does this molecule exhibit optical activity? Explain your answer.

Would you expect carvone to give positive reactions with Tollen's & Fehling's reagents?

4. Draw the structural formula for citral. Does it exhibit geometrical isomerism? Explain.

Would you expect citral to react with sodium borohydride in aq-alc? If so, draw the structure of the product.

If you were to obtain IR spectra of carvone and citral what would be the major differences in the spectra?

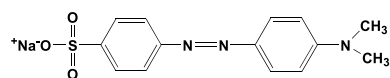
5. When benzene is heated with a mixture of concentrated nitric and sulphuric acids, nitrobenzene is produced.. Write the name and formula of the electrophile in this reaction. Write the formula of the sigma complex transition state and explain the term resonance hybrid.



6. Sulphanilic acid (4-aminobenzenesulphonic acid) can be made by heating benzenamine (aniline) with oleum at  $180^{\circ}\text{C}$ . It is readily converted into the sodium salt (sodium 4-aminobenzenesulphonate) by reaction with sodium hydroxide. Suggest how this substance could be converted into methyl orange.

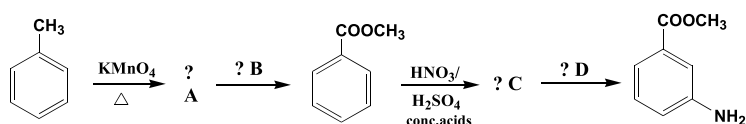
(Hint: you will need to use a diazonium compound and a suitable tertiary amine)

Methyl orange has the structure:

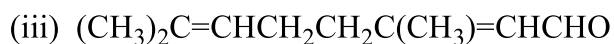
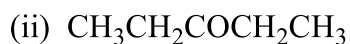


Write formulae showing the overall scheme.

7. Complete and identify the following:



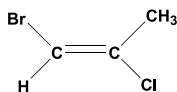
8. Name the following:



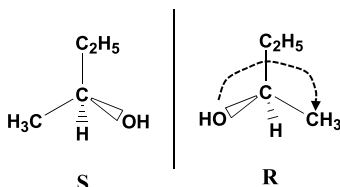
9. An alcohol contains four carbon atoms. It gives a yellow crystalline solid when treated with iodine in aqueous sodium hydroxide. When oxidised it forms a volatile liquid which gives a yellow-orange precipitate with 2,4-dinitrophenylhydrazine. Name the alcohol and explain the reaction.s.

## Homework No 12: Organic Chemistry III (answers)

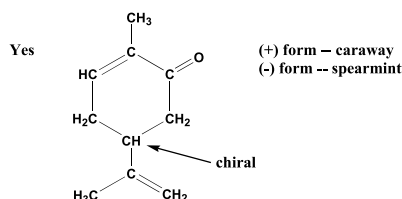
1. Write a structural formula for, E-1-bromo-2-chloropropene.



2. Draw structural formulae for the enantiomers of butan-2-ol. Indicate on your formulae which is the S-form and which the R-form.



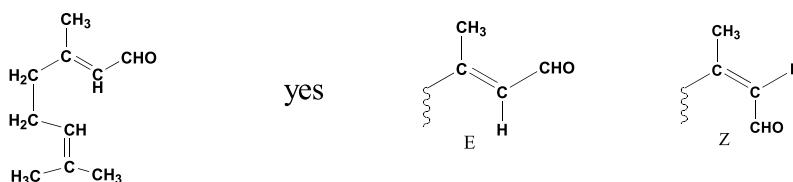
3. Draw a structural formula for carvone. Does this molecule exhibit optical activity? Explain your answer.



Would you expect carvone to give positive reactions with Tollen's & Fehling's reagents?

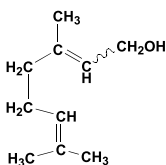
No, because it is a ketone not an aldehyde

4. Draw the structural formula for citral. Does it exhibit geometrical isomerism? Explain.



Would you expect citral to react with sodium borohydride in aq-alc? If so, draw the structure of the product.

Yes

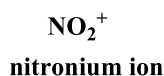


If you were to obtain IR spectra of carvone and citral what would be the major differences in the spectra?

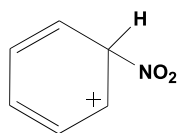
Citral shows absorption at  $2750\text{ cm}^{-1}$  due to aldehydic C-H stretch.

Carvone shows absorption at  $3080\text{ cm}^{-1}$  due to C-H stretch in  $\text{CH}_2=\text{C}$ : & no absorption at  $2750\text{ cm}^{-1}$

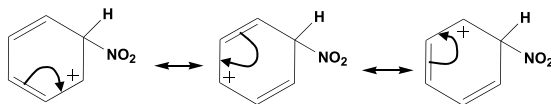
5. When benzene is heated with a mixture of concentrated nitric and sulphuric acids, nitrobenzene is produced.. Write the name and formula of the electrophile in this reaction. Write the formula of the sigma complex transition state and explain the term resonance hybrid.



continued:



$\sigma$  complex



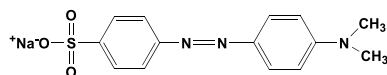
resonance stabilised

The complex has a structure represented by & having the characteristics of, these various canonical forms.

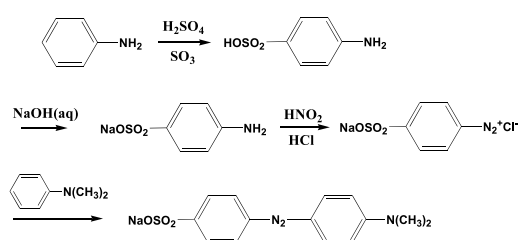
6. Sulphanilic acid (4-aminobenzenesulphonic acid) can be made by heating benzenamine (aniline) with oleum at  $180^{\circ}\text{C}$ . It is readily converted into the sodium salt (sodium 4-aminobenzenesulphonate) by reaction with sodium hydroxide. Suggest how this substance could be converted into methyl orange.

(Hint: you will need to use a diazonium compound and a suitable tertiary amine)

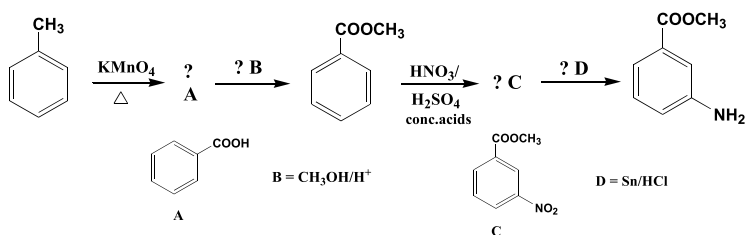
Methyl orange has the structure:



Write formulae showing the overall scheme.



7. Complete and identify the following:



8. Name the following:

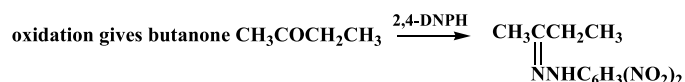
(i)  $\text{CH}_3\text{CH}_2\text{CHO}$       propanal

(ii)  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$       pentan-3-one

(iii)  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$       3,7-dimethyloct-2,6-dienal

9. An alcohol contains four carbon atoms. It gives a yellow crystalline solid when treated with iodine in aqueous sodium hydroxide. When oxidised it forms a volatile liquid which gives a yellow-orange precipitate with 2,4-dinitrophenylhydrazine. Name the alcohol and explain the reactions.

yellow solid =  $\text{CHI}_3$     therefore contains  $\text{CH}_3\text{CHOH-}$  & is  $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$



# Theme Thirteen

## Homework No 13: Acid-Base Equilibria

Try answering these questions, the answers are on the pages which follow.

1. Calculate the pH of 0.01M nitric acid.
2. Calculate the pH of 0.2M sodium hydroxide.
3. Calculate the pH of 0.02M barium hydroxide assuming completely dissociated.
4. Estimate the pH of 0.5M sulphuric acid.
5. 50 cm<sup>3</sup> of 0.1M hydrochloric acid was half neutralised with 25 cm<sup>3</sup> of 0.1M sodium hydroxide. What is the pH of the final solution?

6. What are the **two** most important properties of a buffer solution?

If you were given a buffer solution made up by mixing equal volumes of 1M ethanoic acid and 1M sodium ethanoate what would you expect its pH to be (approximately)? Explain.

If a small amount of dilute hydrochloric acid was added to this solution the pH would remain more or less constant. Explain why the pH does not decrease.

Sketch the changes in pH during the titration of 25cm<sup>3</sup> 0.1M sodium hydroxide with 0.1M ethanoic acid.

Which indicator would you use for the above titration? Explain.

7. For an indicator,  $\text{HIn(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{In}^-(\text{aq})$

$$\text{Indicator constant (K}_{\text{ind}}) = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

Suppose a solution is made by mixing 50.00 cm<sup>3</sup> 1M HCl and 50.10 cm<sup>3</sup> 1M NaOH. A few drops (say 3) of phenolphthalein are added to the mixture. What proportion of the indicator will be converted to the coloured form (In<sup>-</sup>)? The ionic product of water is 10<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>

$$K_{\text{In}} = 10^{-10} \text{ mol dm}^{-3}$$

## Homework No 13: Acid-Base Equilibria (answers)

1. Calculate the pH of 0.01M nitric acid.

The acid is completely dissociated therefore  $\text{pH} = 2$

2. Calculate the pH of 0.2M sodium hydroxide.

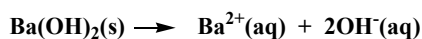
NaOH is completely dissociated therefore hydroxide ion concentration = 0.2M

since,  $10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$

therefore,  $[\text{H}_3\text{O}^+] = (10^{-14}/2) \times 10 = 5 \times 10^{-14} \text{ M}$

therefore,  $\text{pH} = -\log[\text{H}^+] = -(\log 5 \times 10^{-14})$   
 $= 13.3$

3. Calculate the pH of 0.02M barium hydroxide assuming completely dissociated.

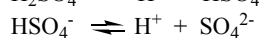


$[\text{OH}^-] = 2 \times 0.02 = 0.04 \text{ M}$

therefore,  $[\text{H}_3\text{O}^+] = (10^{-14}/4) \times 100 = 2.5 \times 10^{-13} \text{ M}$

therefore,  $\text{pH} = -(\log 2.5 \times 10^{-13}) = 12.60$

4. Estimate the pH of 0.5M sulphuric acid.



If  $\text{HSO}_4^-$  was completely undissociated, then  $[\text{H}^+]$  would be entirely due to the first dissociation and,

$[\text{H}^+] = 0.5 \text{ M}$

then,  $\text{pH} = -\log 0.5 = 0.30$

If  $\text{HSO}_4^-$  was completely dissociated then  $[\text{H}^+] = 2 \times 0.5 = 1 \text{ M}$  and  
 $\text{pH} = -\log 1 = 0$

our estimate of pH would be, between 0 & 0.3

(in practice it is 0.29)

5.  $50 \text{ cm}^3$  of 0.1M hydrochloric acid was half neutralised with  $25 \text{ cm}^3$  of 0.1M sodium hydroxide. What is the pH of the final solution?

**$50 \text{ cm}^3$  of 0.1M HCl contains  $(0.05 \times 0.1 = 0.005) \text{ mol HCl}$**

**If this is half neutralised 0.0025 mol remain.**

**This is contained in  $(50 + 25) \text{ cm}^3$  of aq solution.**

**Therefore  $[\text{H}^+] = 1000/75 \times 0.0025 = 0.0333 \text{ M}$**

**Therefore,  $\text{pH} = -\log 0.0333 = 1.477$**

6. What are the **two** most important properties of a buffer solution?

Its pH remains more or less constant when small amounts of acid or alkali are added to it. Also, its pH changes very little when the buffer is diluted with water.

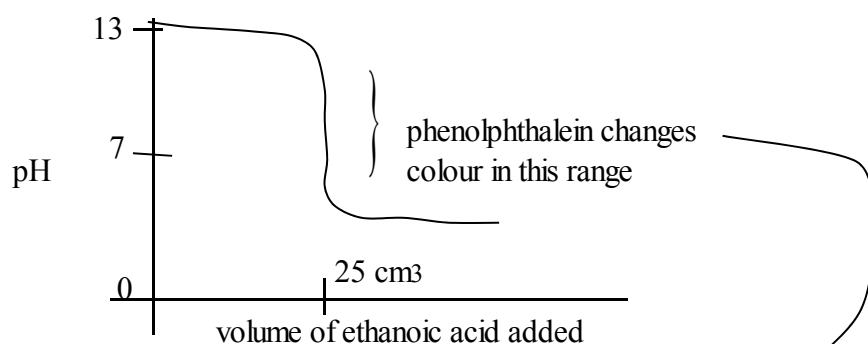
If you were given a buffer solution made up by mixing equal volumes of 1M ethanoic acid and 1M sodium ethanoate what would you expect its pH to be (approximately)? Explain.

Ethanoic acid is a weak acid. It dissociates to a small extent giving ethanoate ions & hydrogen ions. In the given mixture there will be a small concentration of hydrogen ions making it slightly acidic (ie, less than 7, possibly 5).

If a small amount of dilute hydrochloric acid was added to this solution the pH would remain more or less constant. Explain why the pH does not decrease.

The hydrogen ions provided by the strong acid, HCl, are rapidly taken up by ethanoate ions to provide undissociated ethanoic acid molecules. It follows therefore that the mixture does not become more acidic. The pH remains about constant.

Sketch the changes in pH during the titration of 25cm<sup>3</sup> 0.1M sodium hydroxide with 0.1M ethanoic acid.



Which indicator would you use for the above titration? Explain.

7. For an indicator,  $\text{HIn(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{In}^-(\text{aq})$

$$\text{Indicator constant (K}_{\text{ind}}) = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

Suppose a solution is made by mixing 50.00 cm<sup>3</sup> 1M HCl and 50.10 cm<sup>3</sup> 1M NaOH. A few drops (say 3) of phenolphthalein are added to the mixture. What proportion of the indicator will be converted to the coloured form (In<sup>-</sup>)? The ionic product of water is 10<sup>-14</sup> mol<sup>2</sup> dm<sup>-6</sup>

$$K_{\text{In}} = 10^{-10} \text{ mol dm}^{-3}$$

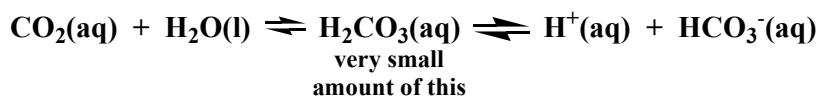
50cm<sup>3</sup> 1M HCl + 50.1cm<sup>3</sup> 1M NaOH, ie, 0.1 cm<sup>3</sup> 1M NaOH in 100 cm<sup>3</sup> of solution.

$$[\text{OH}^-] = \frac{0.1 \times 1 \times 10}{1000} = 10^{-3} \text{ M}$$

$$\text{therefore, } [\text{H}^+] = 10^{-14}/10^{-3} = 10^{-11} \text{ M}$$

$$[\text{In}^-]/[\text{HIn}] = 10^{-10}/10^{-11} = 10/1$$

8. Human blood contains a number of buffering agents which effectively maintain its pH at about 7.4. A simple but important blood buffer is the *carbonic acid* buffer which can be represented,



If the blood plasma was to experience a sudden increase in hydroxyl ion concentration how would this buffer bring return the pH to the optimal 7.4 value?

Hydroxide ion would combine with hydrogen ion forming water. The equilibrium would shift to the right so that carbonic acid would dissociate. This, in turn, would temporarily reduce the amount of carbon dioxide in the plasma. The pH would return to near normal (about 7.4).

An English athlete from London is due to enter a marathon race in Nepal. He is planning to arrive a couple of days before the event. On the big day, after a mile or two into his running, he is aware that his breathing is faster and more laboured than normal and he is experiencing some headache and sickness. He has difficulty concentrating and wants to pull out. How can you explain this in terms of his blood chemistry? If you were his trainer, on the side lines, what would be your advice to the athlete?

He is suffering oxygen starvation because he is not used to the more rarified atmosphere at high altitude. The partial pressure of oxygen in the atmosphere is lower than he is used to. He breaths faster than normal to get more oxygen. He expires carbon dioxide at a faster rate. This raises his blood pH which results in a more sluggish release of oxygen at the muscles.

The advice from his coach and trainer would be to pull out or at least slow down. See what effect slowing down has. If he still feels unwell, pull out of the race all together!

Due to lack of preparation at high altitude he was probably doomed to failure!



# Theme Fourteen

## Homework No 14: Redox Equilibria

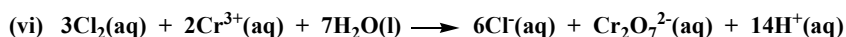
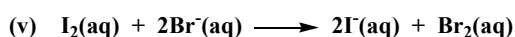
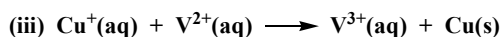
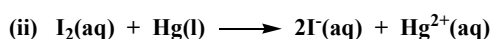
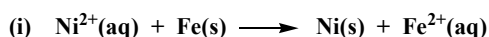
You may refer to the following electrode potentials and those in data books to answer the questions.

Half-cell Reaction	Standard Electrode Potential / V
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Co}(\text{s})$	-0.28
$\text{Cr}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.41
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Ni}(\text{s})$	-0.25
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{V}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.22
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Ag}(\text{s})$	+0.81
$\text{Br}_2(\text{aq}) + 2\text{e}^{-} \rightleftharpoons 2\text{Br}^{-}(\text{aq})$	+1.09
$\text{Cl}_2(\text{g}) + 2\text{e}^{-} \rightleftharpoons 2\text{Cl}^{-}(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^{+}(\text{aq}) + 6\text{e}^{-} \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{Cu}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$	+0.52
$\text{F}_2(\text{g}) + 2\text{e}^{-} \rightleftharpoons 2\text{F}^{-}(\text{aq})$	+2.87
$\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Hg}(\text{l})$	+0.85
$\text{I}_2(\text{aq}) + 2\text{e}^{-} \rightleftharpoons 2\text{I}^{-}(\text{aq})$	+0.54
$\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e}^{-} \rightleftharpoons 4\text{H}_2\text{O}(\text{l}) + \text{Mn}^{2+}(\text{aq})$	+1.51
$\text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{S}(\text{s}) + 2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{H}_2\text{O}(\text{l})$	+0.14

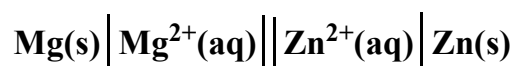
1. An iron nail is dipped into a 1M solution of silver nitrate.  
Is there likely to be a reaction? Explain in terms of standard electrode potentials.

If you predict that a reaction *is* likely, write an overall chemical equation for the reaction.

2. Using standard electrode potential values, predict which of the following reactions can take place.



3. An electrochemical cell is represented by the following shorthand:



$$E_{\text{cell}}^{\ominus} = +1.61 \text{ V}$$

(i) Draw a sketch showing how this cell could be constructed in the laboratory.

(ii) If the cell was connected to a small torch bulb which way would the current flow through the bulb (magnesium to zinc or zinc to magnesium)? Write a balanced chemical equation for the reaction.

3. Continued:

(iii) The value  $+1.61\text{ V}$  is the cell EMF. What do the letters EMF stand for? In the laboratory what device is used to measure the EMF?

(iv) Show how the cell EMF can be calculated from the individual standard electrode potentials.

4. Which of the metals, silver, zinc or magnesium might be coated with lead when immersed in a solution of lead nitrate. Explain your answer.

5. The cell represented in question 3, above, has a ***salt bridge***. Briefly explain the function of the salt bridge, supposing it to be a strip of filter paper which has been soaked in potassium nitrate solution.

## Homework No 14: Redox Equilibria (answers)

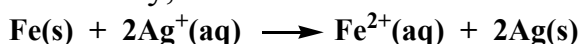
Half-cell Reaction	Standard Electrode Potential / V
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.41
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Co}(\text{s})$	-0.28
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Ni}(\text{s})$	-0.25
$\text{V}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.22
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{S}(\text{s}) + 2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{H}_2\text{O}(\text{l})$	+0.14
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{Cu}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$	+0.52
$\text{I}_2(\text{aq}) + 2\text{e}^{-} \rightleftharpoons 2\text{I}^{-}(\text{aq})$	+0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Ag}(\text{s})$	+0.81
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Hg}(\text{l})$	+0.85
$\text{Br}_2(\text{aq}) + 2\text{e}^{-} \rightleftharpoons 2\text{Br}^{-}(\text{aq})$	+1.09
$\text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^{+}(\text{aq}) + 6\text{e}^{-} \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{Cl}_2(\text{g}) + 2\text{e}^{-} \rightleftharpoons 2\text{Cl}^{-}(\text{aq})$	+1.36
$\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5\text{e}^{-} \rightleftharpoons 4\text{H}_2\text{O}(\text{l}) + \text{Mn}^{2+}(\text{aq})$	+1.51
$\text{F}_2(\text{g}) + 2\text{e}^{-} \rightleftharpoons 2\text{F}^{-}(\text{aq})$	+2.87

1. An iron nail is dipped into a 1M solution of silver nitrate.

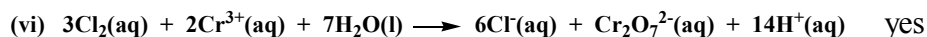
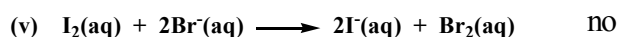
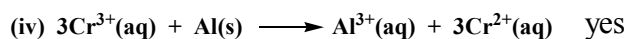
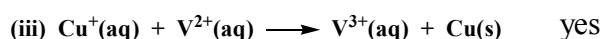
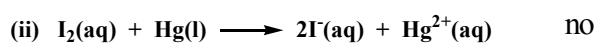
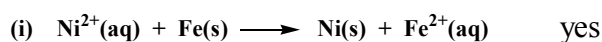
Is there likely to be a reaction? Explain in terms of standard electrode potentials.

*Yes. The iron/iron(II) system has the more negative electrode potential (-0.4V). It will reduce the silver/silver(I) system converting silver(I) to silver metal. Finely divided silver metal will collect on the iron nail.*

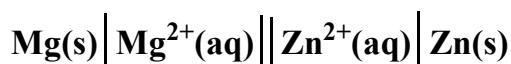
If you predict that a reaction is likely, write an overall chemical equation for the reaction.



2. Using standard electrode potential values, predict which of the following reactions can take place.

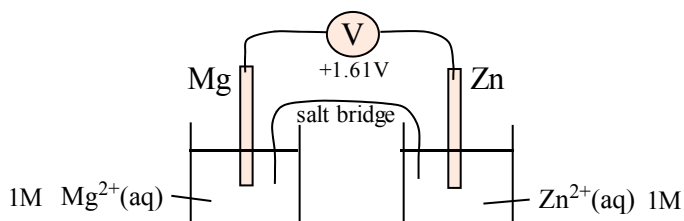


3. An electrochemical cell is represented by the following shorthand:



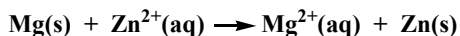
$$E_{\text{cell}}^{\ominus} = +1.61 \text{ V}$$

(i) Draw a sketch showing how this cell could be constructed in the laboratory.



(ii) If the cell was connected to a small torch bulb which way would the current flow through the bulb (magnesium to zinc or zinc to magnesium)? Write a balanced chemical equation for the reaction.

*The electron flow would be from the magnesium electrode to the zinc electrode. This is because magnesium has a more negative electrode potential than zinc.*



3. Continued:

(iii) The value +1.61 V is the cell EMF. What do the letters EMF stand for? In the laboratory what device is used to measure the EMF?

EMF = ElectroMotive Force.

Emf can be measured using an electrostatic voltmeter (high resistance voltmeter).

(iv) Show how the cell EMF can be calculated from the individual standard electrode potentials.

$$E_{\text{cell}}^{\ominus} = E_{\text{right}}^{\ominus} - E_{\text{left}}^{\ominus} = -0.76 - (-2.37) \text{ V} = +1.61 \text{ V}$$

4. Which of the metals, silver, zinc or magnesium might be coated with lead when immersed in a solution of lead nitrate. Explain your answer.

*zinc and magnesium.*

*These two metals are more reactive than lead. They have more negative electrode potentials than lead. This means that if you were to dip either zinc or magnesium strips into lead nitrate solution, lead metal would be deposited on the strip. The metal comprising the strip gradually ionises and goes into solution.*

*In the case of a strip of silver, it would remain unchanged when introduced into the lead nitrate solution.*

5. The cell represented in question 3, above, has a **salt bridge**. Briefly explain the function of the salt bridge, supposing it to be a strip of filter paper which has been soaked in potassium nitrate solution.

**Salt bridge:** *provides an electrical connection between the two half cells without allowing the solutions to mix.*

*It can allow movement of ions between the two half cells but if the cell is not providing current the flow of ions through the bridge is zero.*

# Theme Fifteen

## Homework No 15: Industrial Chemistry

Try answering these questions, the answers are on the pages which follow.

1. The industrial process for making sulphuric acid is called the **contact process**. It basically involves three stages. Describe the contact process giving chemical equations and reaction conditions.
2. In terms of the amount produced world-wide, sulphuric acid is the fifth most important inorganic chemical (cement being the most important!).
  - (a) What is the main application of sulphuric acid?
  - (b) A couple of smaller industrial applications of sulphuric acid are in *pickling* and *anodising*. Explain what these processes involve.
3.
  - (a) What is the chemical composition of superphosphate?
  - (b) How is it made and what is it used for?
4. ( a) Draw a labelled sketch of the *membrane cell* used to manufacture chlorine.

[Continued:](#)

4. (b) Write an equation to represent the reaction at the **anode** in the membrane cell.

(c) What are the other important industrial products from the membrane cell?

(d) State three important uses of chlorine.

5. Sodium chlorate(I) disproportionates when warmed in aqueous solution. Explain what this means and write an equation giving oxidation numbers.

6. (a) What materials are required to produce strike-anywhere matches? (b) How can the strike - anywhere match be modified to make it safer?

7. The first stage in the manufacture of nitric acid is the oxidation of ammonia to nitrogen(II) oxide. ( a) Write an equation for this reaction and state the operating conditions.

(b) The second stage in the manufacture involves oxidising nitrogen(II) oxide to nitrogen(IV) oxide.

( c) Write an equation for the oxidation. State the colours of the oxides.

(d) In the third stage nitrogen(IV) oxide is reacted with water to give nitric acid. Give the equation.



8. The main commercial application of nitric acid is in manufacture of fertilizers. (a) Name one fertilizer manufactured using nitric acid. Represent its formation by writing equations.

(b) Give an example of a *compound fertilizer*.

(c) What is aqua regia? What can be achieved with aqua regia that is not possible to achieve with the individual strong mineral acids?

9. Aluminium is the most abundant metal in the earth crust. ( a) Why, therefore, is it not the cheapest metal to produce commercially?

(b) Outline how aluminium is manufactured. State the main ore and write chemical equations to explain the processes.

10. ( a) What is the main constituent of the ore, haematite? (b) What colour is the ore?

( c) In the extraction of iron from oxides of iron, carbon monoxide is used as reducing agent. Give an example of this by writing a suitable equation.

(d) Crushed limestone is also used in the extraction process. Explain the purpose of this.

(e) What is the difference between *cast iron* and *wrought iron*?

10. (continued). (f) In relation to steel manufacture explain the terms, *quenching* and *annealing*.

12. (a) Define the term *transition element*.

(b) Copper is a transition element. State three properties of copper which make it a typical transition element.

(c) What is the chemical composition of malachite?

(d) Suggest a way of converting malachite to copper metal in the laboratory.

(e) Chalcopyrites is the most common ore of copper. What is the chemical composition of this ore?

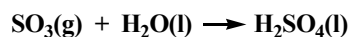
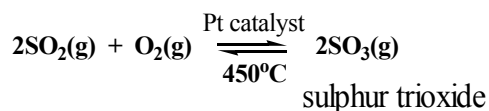
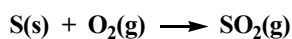
(f) Write equations showing how copper metal is obtained from the crushed and purified ore.

(g) Explain how impure blister copper can be converted to very pure copper suitable for the electrical industry.

State two uses of copper other than as a conductor of electricity.

## Homework No 15: Industrial Chemistry (answers)

1. The industrial process for making sulphuric acid is called the **contact process**. It basically involves three stages. Describe the contact process giving chemical equations and reaction conditions.



2. In terms of the amount produced world-wide, sulphuric acid is the fifth most important inorganic chemical (cement being the most important!). (a) What is the main application of sulphuric acid?

Used for the manufacture of fertilizers

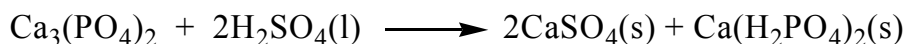
(b) A couple of smaller industrial applications of sulphuric acid are in *pickling* and *anodising*. Explain what these processes involve.

Pickling involves cleaning metal by immersion in dilute sulphuric acid to remove the oxide coat.

Anodising is an electrolytic process in which aluminium is made the anode in dilute sulphuric acid electrolyte.

Oxygen, liberated at the anode, oxidises the surface metal to produce a tough oxide coat which can be dyed.

3. (a) What is the chemical composition of superphosphate?

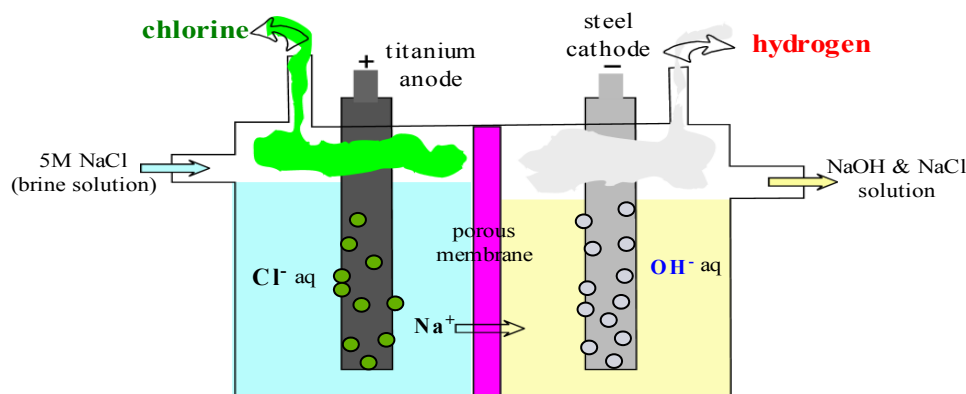


(b) How is it made and what is it used for?

Unlike phosphate rock, the dihydrogenphosphate is soluble in water. It is washed into the soil when it rains and is taken up by the roots of the plants so providing the phosphorus they need.



4. (a) Draw a labelled sketch of the *membrane cell* used to manufacture chlorine.



Continued:-

4. (b) Write an equation to represent the reaction at the **anode** in the membrane cell.

**At the anode (+):**



(c) What are the other important industrial products from the membrane cell?

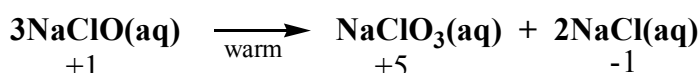
Hydrogen and sodium hydroxide (caustic soda)

(d) State three important uses of chlorine.

1. Manufacture of chloroethene to make PVC.
2. Manufacture of hydrogen chloride to make hydrochloric acid.
3. Manufacture of sodium chlorate(I) .

5. Sodium chlorate(I) disproportionates when warmed in aqueous solution. Explain what this means and write an equation giving oxidation numbers.

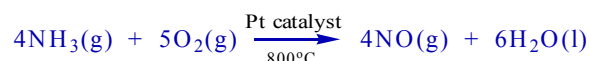
This is where an element (chlorine in this case) undergoes a reaction in which it is oxidised and reduced.



6. (a) What materials are required to produce strike-anywhere matches? (b) How can the strike - anywhere match be modified to make it safer?

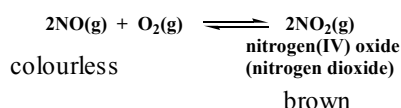
These match heads contain phosphorus trisulphide ( $\text{P}_4\text{S}_3$ ), potassium chlorate(V) ( $\text{KClO}_3$ ), starch, siliceous filler and glue. Friction on a rough surface causes a vigorous, exothermic, reaction between the sulphide and the chlorate which generates sufficient heat to combust the wood match stick. A safer match is made by excluding the sulphide from the match head and replacing it with a little sulphur and antimony sulphide ( $\text{Sb}_2\text{S}_3$ ). The striking surface (ie, the side of the match box) contains red phosphorus and powdered glass. When the match head is struck against the surface, reactions involving phosphorus, sulphur and chlorate occur generating heat to ignite the match stick.

7. The first stage in the manufacture of nitric acid is the oxidation of ammonia to nitrogen(II) oxide. ( a) Write an equation for this reaction and state the operating conditions.

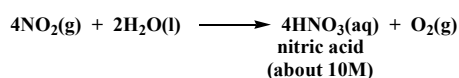


The second stage in the manufacture involves oxidising nitrogen(II) oxide to nitrogen(IV) oxide.

( b) Write an equation for the oxidation. State the colours of the oxides.

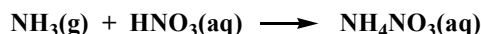


(c) In the third stage nitrogen(IV) oxide is reacted with water to give nitric acid. Give the equation.



8. The main commercial application of nitric acid is in manufacture of fertilizers. (a) Name one fertilizer manufactured using nitric acid. Represent its formation by writing equations.

Ammonium nitrate



(b) Give an example of a *compound fertilizer*.

A mixture of ammonium phosphate and ammonium nitrate

(c) What is aqua regia? What can be achieved with aqua regia that is not possible to achieve with the individual strong mineral acids?

Aqua regia is a mixture of 25% concentrated nitric acid and 75% concentrated hydrochloric acid. It dissolves gold.

9. Aluminium is the most abundant metal in the earth crust. (a) Why, therefore, is it not the cheapest metal to produce commercially?

Most aluminium occurs in aluminosilicates (in soil and rocks) from which it would be very difficult and expensive to extract the metal. Instead, the metal is extracted from bauxite which is much easier to process. Another factor is that the electrolytic stage, in which the metal is extracted from its oxide, is expensive to operate.

(b) Outline how aluminium is manufactured. State the main ore and write chemical equations to explain the processes.

1. **Purification** of bauxite to give alumina ( $\text{Al}_2\text{O}_3$ ).

2. **Electrolysis** of a solution of alumina in a mixture of molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) and aluminium fluoride ( $\text{AlF}_3$ ).

**Purification** is necessary because bauxite contains various other oxides which must be removed in order for the subsequent electrolysis to be successful.

In some cases the bauxite ore may contain as little as 50%  $\text{Al}_2\text{O}_3$  and possibly, 25%  $\text{Fe}_2\text{O}_3$  and variable amounts of  $\text{SiO}_2$  and  $\text{TiO}_2$ .

The bauxite ore is crushed and then digested with hot sodium hydroxide solution. The

reacts forming soluble aluminate.  $\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O} \longrightarrow 2\text{NaAl}(\text{OH})_4(\text{aq})$  sodiumaluminate(III)

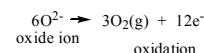
The basic oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , do not dissolve in the alkali and can be filtered off.

The  $\text{SiO}_2$  is a slightly acidic oxide and reacts forming soluble silicate.

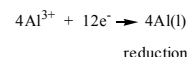
The alkaline solution is cooled, agitated with compressed air and seeded with a little aluminium hydroxide. This causes hydrated aluminium hydroxide to precipitate. It is filtered off and then heated to about  $1000^\circ\text{C}$  to drive off water and leave pure aluminium oxide (alumina).  $2\text{Al}(\text{OH})_3(\text{s}) \longrightarrow 2\text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l})$

Silicon, as silicate, remains behind in the alkaline solution.

At the Anode:



At the Cathode:



10. (a) What is the main constituent of the ore, haematite? (b) What colour is the ore?

$\text{Fe}_2\text{O}_3$       reddish-brown

(c) In the extraction of iron from oxides of iron, carbon monoxide is used as reducing agent. Give an example of this by writing a suitable equation.



(d) Crushed limestone is also used in the extraction process. Explain the purpose of this.

In the furnace it decomposes giving calcium oxide and carbon dioxide. The oxide combines with sandy impurities to give *slag* and the carbon dioxide is reduced by carbon to carbon monoxide.

(e) What is the difference between *cast iron* and *wrought iron*?

Cast iron contains a high proportion of carbon (about 4%) & other impurities. It is brittle. Wrought iron is purer & contains much less carbon (less than 0.5%). It is relatively soft and malleable.

10. (continued). (f) In relation to steel manufacture explain the terms, *quenching* and *annealing*.

Immersing hot iron in cold water, to harden it, is called quenching.

Reheating the quenched iron to about 250 C and allowing it to cool slowly is called tempering or annealing.

It is designed to soften the iron a little.

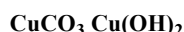
12. (a) Define the term *transition element*.

Elements which have partly filled d-levels in one or more of their oxidation states.

(b) Copper is a transition element. State three properties of copper which make it a typical transition element.

1. It has more than one oxidation state (2 common ones Cu(I) & Cu(II) ) and forms a large number of compounds.
2. Some of these compounds are coloured (mostly green and blue).
3. It forms complex ions.

(c) What is the chemical composition of malachite?



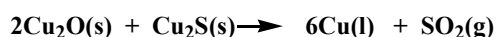
(d) Suggest a way of converting malachite to copper metal in the laboratory.

Heat to give the oxide (CuO) and reduce this by heating in hydrogen (or methane from the gas supply).

(e) Chalcopyrites is the most common ore of copper. What is the chemical composition of this ore?

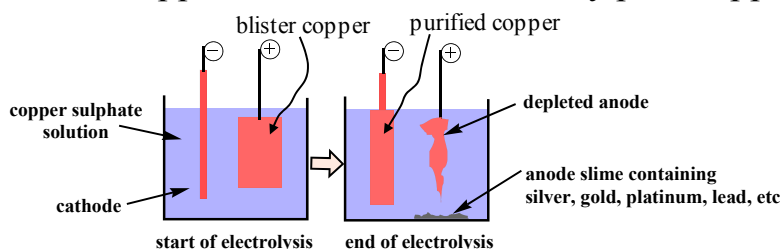


(f) Write equations showing how copper metal is obtained from the crushed and purified ore.



(g) Explain how impure blister copper can be converted to very pure copper suitable for the electrical industry.

By electrolysis



State two uses of copper other than as a conductor of electricity.

1. Conductor of heat as in central heating systems.
2. Manufacture of metal coins and decorative plaques, plates and sculptures.

# Theme Sixteen

## Homework No 16: Organic Analysis

1.

A chemistry student was given an impure organic substance to analyse. The following details were entered in her practical book.

“A known quantity of the crude material was dissolved in ether and this solution washed with 2M KOH (2x30 cm<sup>3</sup>). The phases were separated and the ether phase washed with 2M HCl (2x30 cm<sup>3</sup>). The ether phase was again separated, dried and evaporated to remove all of the ether; a crystalline residue (A) was obtained. Acidification of the alkaline aqueous phase did not produce any organic material. Neutralisation of the HCl phase did not produce organic material.”

The student continued with the examination of the isolated substance (A). The substance was recrystallised from IMS/water (1:1), dried, and a melting point and infra-red spectrum obtained. Substance (A) melted at 125°C and its ir spectrum showed three medium sized, sharp, peaks in the region 3010-3070 cm<sup>-1</sup>. Strong absorption was observed at 1600, 1500 and 1450 cm<sup>-1</sup>. The pmr spectrum of A shows a singlet at 7.15 ppm and a complex multiplet between 7.21 & 7.48 ppm.

Substance (A) slowly decolourised bromine water and potassium permanganate solutions. Boiling with more concentrated, acid, permanganate produced benzoic acid and traces of benzenecarbaldehyde. All other functional group tests proved negative. The Lassaigne test gave negative results.

Quantitative analysis showed that 1.80 g of substance (A) produced 6.16 g of carbon dioxide and 1.08 g of water on complete combustion.

Interprete the above results.

Calculate the empirical formula of (A). Use this with your other conclusions to write a possible structural formula for (A). Name the substance you write a formula for.

Explain how pmr spectroscopy of (A) would help to confirm its identity.

[Continued:](#)

2.

Substance (A) is a white crystalline solid. It is sparingly soluble in water giving a slightly acidic solution.

It dissolves in dilute KOH and gives carbon dioxide with aqueous sodium carbonate. Element analysis reveals that (A) contains 60% carbon, 4.4% hydrogen and 35.6% oxygen. When substance (A) is refluxed with excess dilute KOH and the resulting solution acidified a white crystalline solid (B) precipitates. Substance (B) gives a purple colour with iron(III) chloride solution and when heated with soda-lime it gives benzenol (phenol).

The IR spectrum of substance (A) shows broad absorption between  $3500 - 2600\text{ cm}^{-1}$  and two intense absorption peaks at  $1750\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ . The IR spectrum of substance (B) shows only one peak in the region of  $1700\text{ cm}^{-1}$ .

The PMR spectrum of (A) shows a singlet at 2.35 ppm, a broad singlet at 11.30 ppm and a group of four peaks between 8.2 and 7.1 ppm each of which is either a doublet or triplet.

Identify substances (A) and (B) and show how the above information corresponds with your proposed structures.

What further analyses would you perform to confirm your structures?

Continued:-



## Homework No. 16: Organic Analysis (Answers)

1.

A neutral substance separated, ie, not acidic or basic.

No common functional groups therefore a hydrocarbon.

No nitrogen, sulphur or halogen.

Unsaturated and probably aromatic as evidenced by infra-red & chemical tests.

Conjugated, unreactive, carbon-carbon bond.

<u>C</u>	<u>H</u>
1.68	0.12
1.68/12	0.12/1
= 0.14	= 0.12

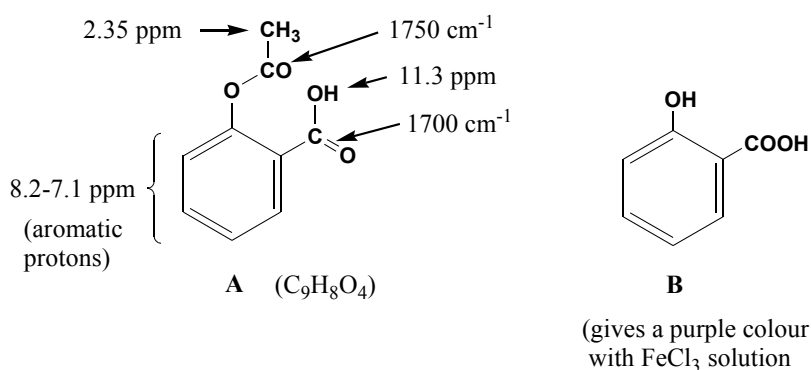
ie,  $\frac{C}{H} = \frac{14}{12}$   
 $\frac{7}{6}$   
EF = C<sub>7</sub>H<sub>6</sub>

If aromatic then, C<sub>6</sub>H<sub>5</sub>CH, therefore probably, C<sub>6</sub>H<sub>5</sub>CH=CHC<sub>6</sub>H<sub>5</sub> (stilbene, 1,2-diphenylethene)

This would react slowly with bromine water and aqueous permanganate and would give benzaldehyde and benzoic acid with acid permanganate.

The pmr would show a singlet due to the central CH= protons and a complex of peaks corresponding to the aromatic protons (7.21 - 7.48 ppm).

2.



**Further analyses:** measure the melting points of A and B. Substance A is acetylsalicylic acid (aspirin) and melts at 135°C. Substance B is 2-hydroxybenzenecarboxylic acid (salicylic acid) and melts at 155°C. Substance A reacts with ethanol to give the ethyl ester which boils at 272°C. Substance B gives 5-nitrosalicylic acid when warmed with 15% nitric acid; this melts at 226°C.